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<b>(21) International Application Number:</b> PCT/US97/05539 <b>(22) International Filing Date:</b> 4 April 1997 (04.04.97)  <b>(30) Priority Data:</b> 08/651,077      22 May 1996 (22.05.96)      US 08/700,974      21 August 1996 (21.08.96)      US  <b>(71) Applicant:</b> BETZDEARBORN INC. [US/US]; 4636 Somerton Road, Trevose, PA 19053-6783 (US). <b>(72) Inventor:</b> NGUYEN, Duy, T.; 9186 Spindle Tree Way, Jacksonville, FL 32256 (US). <b>(74) Agents:</b> VON NEIDA, Philip, H. et al.; BetzDearborn Inc., 4636 Somerton Road, Trevose, PA 19053-6783 (US).		<b>(81) Designated States:</b> AU, CA, JP, KR, NO, NZ, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> COMPOSITIONS AND METHODS FOR INHIBITING DEPOSITS IN PULP AND PAPERMAKING SYSTEMS		
<b>(57) Abstract</b> <p>Compositions and methods for inhibiting the deposition of organic contaminants from pulp in pulp and papermaking systems are disclosed. The methods add to the pulp or to the deposition prone surface of the papermaking system a composition comprising a polyvinyl alcohol having 50 to 100 % hydrolysis, a high molecular weight gelatin having a molecular weight of about 100,000 or higher, and a cationic polymer.</p>		

**COMPOSITIONS AND METHODS FOR INHIBITING DEPOSITS IN PULP AND PAPERMAKING SYSTEMS**

This application is a continuation-in-part of application Serial No. 08/651,077 filed May 22, 1996 which is a continuation-in-part of application Serial No. 08/421,349 filed April 12, 1995, now U.S. Pat. No. 5,536,363.

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**FIELD OF THE INVENTION**

The present invention relates to compositions and methods for inhibiting the deposition of organic contaminants in pulp and paper-making systems.

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**BACKGROUND OF THE INVENTION**

The deposition of organic contaminants in the pulp and paper industry can cause both quality and efficiency problems in pulp and paper-making systems. Some components occur naturally in wood and are released during various pulping and papermaking processes. The term "pitch" can be used to refer to deposits composed of organic constituents

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The deposition of organic contaminants can be detrimental to the efficiency of a pulp or paper mill causing both reduced quality and reduced operating efficiency. Organic contaminants can deposit on process equipment in papermaking systems resulting in operational difficulties in the systems. The deposition of organic contaminants on consistency regulators and other instrument probes can render these components useless. Deposits on screens can reduce throughput and upset operation of the system. This deposition can occur not only on metal surfaces in the system, but also on plastic and synthetic surfaces such as machine wires, felts, foils, Uhle boxes and headbox components.

Historically, the subsets of the organic deposit problems, "pitch" and "stickies" have manifested themselves separately, differently and have been treated distinctly and separately. From a physical standpoint, "pitch" deposits have usually formed from microscopic particles of adhesive material (natural or man-made) in the stock which accumulate on papermaking or pulping equipment. These deposits can readily be found on stock chest walls, paper machine foils, Uhle boxes, paper machine wires, wet press felts, dryer felts, dryer cans, and calendar stacks. The difficulties related to these deposits included direct interference with the efficiency of the contaminated surface, therefore, reduced production, as well as holes, dirt, and other sheet defects that reduce the quality and usefulness of the paper for operations that follow like coating, converting or printing.

strategies which will be highly effective at eliminating both of these problems without having to feed two or more separate chemicals. The materials of this invention have clearly shown their ability to achieve this goal.

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### **SUMMARY OF THE INVENTION.**

The present invention provides for compositions and methods for inhibiting the deposition of organic contaminants from pulp in pulp and  
10 papermaking systems. The methods comprise adding to the pulp or the surfaces of the papermaking machinery a composition comprising polyvinyl alcohol, a high molecular weight gelatin, and a cationic polymer.

### **DESCRIPTION OF THE RELATED ART**

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U.S. Patent No. 4,871,424 teaches methods for controlling pitch deposition from pulp in papermaking systems utilizing a water-soluble polyvinyl alcohol having 50% to 100% hydrolysis. U.S. patent No. 4,886,575 teaches a method for inhibiting the deposition and adherency  
20 of hot melt and/or pressure sensitive adhesive materials, "stickies", on the surfaces of repulping equipment using polyvinyl alcohol moieties that also contain some hydrophobic groupings, these PVA moieties having 70 to 99% hydrolysis. "Pulp and Paper", by James Casey, Vol. III, 3rd Ed., pp. 1587-1588, teaches that gelatin has been suggested as a remedy for  
25 pitch trouble.

readily commercially available. Representative polyvinyl alcohols include Airvol® 205 (MW≈25,000), Airvol® 523 (MW≈78,000) and Airvol® 540 (MW≈125,000), all available under their respective tradenames from Air Products, Inc.

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The gelatin that is preferred for use in the synergistic composition has a molecular weight ranging from about 100,000 to about 250,000. Most preferably, the gelatin has a molecular weight of about 130,000. One such gelatin is commercially available from Hormel Foods under the tradename Flavorset GP-4. The term "high molecular weight gelatin" is defined as a gelatin having a molecular weight of about 100,000 or higher.

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The cationic polymers useful in the present invention generally are protonated or quaternary ammonium polymers such as the reaction product between an epihalohydrin and one or more amines; polymers derived from ethylenically unsaturated monomers which contain an amine or a quaternary ammonium group; and acrylamide copolymers produced from the reaction of acrylamide and ethylenically unsaturated cationic monomers.

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Such cationic polymers can be derived from the reaction of an epihalohydrin, preferably epichlorohydrin, with dimethylamine, ethylene diamine and a polyalkylene polyamine. Preferred polymers include the reaction product of an epihalohydrin with dimethylamine, diethylamine or methylethylamine. More preferred polymers include polyamine and polyethyleneimine (PEI).

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Non-limiting examples of cationic monomers that can be used in the methods of the present invention include: diallyldiethylammonium chloride; diallyldimethylammonium chloride (DADMAC); acryloyloxyethyltrimethylammonium chloride (AETAC); methacryloyloxyethyltrimethylammonium chloride (METAC); methacrylamidopropyltrimethylammonium chloride (MAPTAC); acrylamidopropyltrimethylammonium chloride (APTAC); acryloyloxyethyltrimethylammonium methosulfate (AETAMS); methacryloyloxyethyltrimethylammonium methosulfate (METAMS); acryloyloxyethyldiethylmethylammonium chloride; methacryloyloxyethyldiethylmethylammonium chloride; methacryloyloxyethyldiethylmethylammonium chloride. Mixtures of the cationic monomers together with acrylamide to prepare the cationic polymers are also useful in this invention. The instant invention also contemplates homopolymers of the cationic monomers, as well as copolymerization of mixtures of cationic monomers without acrylamide as useful. The above description of cationic polymers should not be construed as limiting the practice of this invention.

Surprisingly, it has been found that when the ingredients are mixed, in certain instances, the resulting mixtures possess a higher degree of inhibiting organic deposition than that of the individual ingredients comprising the mixture. Accordingly, it is possible to produce a highly efficacious inhibitor for use in pulp and papermaking systems. Because of the enhanced activity of the mixture, the total quantity of the deposition inhibitor treatment may be reduced. In addition, the high degree of inhibition which is provided by each of the ingredients may be exploited without use of higher concentrations of each.

The compositions of the present invention can be added to the papermaking system at any stage. They may be added directly to the pulp furnish or indirectly to the furnish through the headbox. The inventive compositions may also be sprayed onto surfaces that are suffering  
5 from deposition, such as the wire, press felts, press rolls and other deposition-prone surfaces.

The compositions of the present invention can be added to the papermaking system neat, as a powder, slurry or in solution; the preferred primary solvent being water but is not limited to such. When added  
10 by spraying techniques, the inventive composition is preferably diluted with water to a satisfactory inhibitor concentration. The inventive compositions may be added specifically and only to a furnish identified as contaminated or may be added to blended pulps. The compositions may  
15 be added to the stock at any point prior to the manifestation of the deposition problem and at more than one site when more than one deposition site occurs. Combinations of the above additive methods may also be employed by feeding either the polyvinyl alcohol or high molecular weight gelatin or cationic polymer separately, by way of feeding the pulp mill-  
20 stock, feeding to the paper machine furnish, and spraying on the wire and the felt simultaneously.

The effective amount of the composition to be added to the papermaking system depends on a number of variables including the pH of the  
25 system, hardness of the water, temperature of the water, additional additives, and the organic contaminant type and content of the pulp. Generally, from 0.5 parts to about 150 parts of the inventive composition per

coupon can be fabricated from any type of adhesive tape that will not disintegrate when placed in water. For this study, tapes made from a styrenebutadiene rubber and vinylic esters were used. Both of these potential organic contaminants are known to cause stickies problems in secondary fiber utilization. A second coupon was fabricated from polyester film such as MYLAR<sup>®</sup>, a product marketed by the DuPont Chemical Company. This material was chosen because paper machine forming fabrics are frequently made of polyester which is susceptible to considerable deposition problems caused by stickies and/or pitch.

10

This test involved immersing a 2" x 4" adhesive tape and a 2" x 4" polyester Mylar coupon into a 600 gram solution being tested. The solution contained in a 600 mL beaker is placed in a water bath with agitation and heated to the desired temperature. After 30 minutes of immersion, the tape and coupon are removed from the solution and pressed to 10,000 lb force for one minute. A tensile test instrument (Instron) is then used to measure the force required to pull the two apart. A reduction in the force required indicates that the "stickie" has been detackified. The % control or detackification is calculated by the following equation:

20

$$\% \text{ detackification} = \frac{(\text{untreated force} - \text{treated force})}{\text{untreated force}} \times 100$$

Contact angle measurements were also performed utilizing the inventive composition. The MYLAR or tape adhesive surface is clamped on a film stage and placed inside the glass test cell. The test solution is added to the cell by carefully pouring 15 mL of the solution into the cell. The whole test cell was then placed inside the chamber of a goniometer (Kruss G1). The MYLAR or tape adhesive surface was immersed in the

25



As demonstrated in Table I, the inventive composition of PVA, HMW gelatin and cationic was more effective than PVA, a known inhibitor. Further studies were performed to determine the peel force of various treatments. These results are reported in Table II.

5

**TABLE II**

Southern Tissue Mill White Water  
78°F

10	<u>Treatment (ppm)</u>	<u>Peel Force (lb -f)</u>	
		<u>5 min.</u>	<u>15 min.</u>
	Control	2.291	1.257
	4 (1 ppm)	1.328	0.898
	1 (1 ppm)	0.816	0.246

15

Further contact angle measurements were performed on a different water. These results are presented in Table III.

**TABLE III**

20 Contact angle of MYLAR or wax  
Midwestern Liner Board  
Wilhelmy Plate, 2 second contact time

25	<u>Treatment No. (ppm)</u>	<u>Contact Angle</u>	
		<u>MYLAR (T=78°F)</u>	<u>Wax (T=115°F)</u>
	Control	30.1	17.7
	4 (10)	14.4	13
	1 (10)	7.2	0.5
	4 (20)		15
	1 (20)		0.5

**TABLE VI**

Interfacial Viscosity of  
Treated Midwestern Tissue Mill  
White Water/Oil Interface at 80°F

5	<u>Treatment No. (ppm)</u>	<u>Interfacial Viscosity (S.C.P.)</u>
	Control	0.13
	4 (5)	0.23
	1 (5)	0.39
	4 (10)	0.34
10	1 (10)	0.45

As demonstrated in Table VI, the inventive composition produced a more stable and less likely to deposit solution than PVA by itself. Similar results at a higher temperature are demonstrated in Table VII.

**TABLE VII**

Interfacial Viscosity of  
Treated Midwestern Tissue Mill  
White Water/Oil Interface at 100°F

20	<u>Treatment No. (ppm)</u>	<u>Interfacial Viscosity (S.C.P.)</u>
	Control	0.23
	4 (5)	0.34
	1 (5)	0.47
25	4 (10)	0.36
	1 (10)	0.49

The peel force of this white water was also tested and these results are shown in Table VIII.

**TABLE XI**

Peel Force  
Midwestern Tissue Mill White Water  
120°F

5 Treated Tape for 5 min.

	<u>Treatment No. (ppm)</u>	<u>Peel Force (lb-F)</u>
	Control	2.331
	4 (2)	1.115
10	1 (2)	0.694

Tables VIII-XI demonstrate that the inventive combination of PVA/HMW gelatin/cationic polymer is more effective at detackifying a liner board solution than just PVA alone.

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**TABLE XII**

Interfacial Viscosity  
Midwestern Tissue Mill White Water/Oil Interface  
at 120°F

	<u>Treatment No. (ppm)</u>	<u>Interfacial Viscosity (S.C.P.)</u>
20	Control	0.23
	4 (5)	0.39
	1 (5)	0.49

**TABLE XIII**

25 Effect of Temperature on Interfacial Viscosity  
Midwestern Tissue Mill White Water/Oil Interface

	<u>Treatment No. (ppm)</u>	<u>Interfacial Viscosity (S.C.P.)</u>		
		<u>120°F</u>	<u>80°F</u>	<u>100°F</u>
30	Control	0.23	0.13	0.23
	4 (5)	0.39	0.23	0.34
	1 (5)	0.49	0.39	0.47
	4 (10)	-----	0.36	0.36
	1 (10)	-----	0.45	0.49

Tables XV and XVI demonstrate that the inventive composition provides better inhibition of deposition to a white water solution as shown by the higher interfacial viscosity than the PVA by itself.

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**TABLE XVII**

Peel Force  
Southern Liner Board Solution

	<u>Treatment No. (ppm)</u>	<u>Peel Force (lb-F)</u>	
		<u>123°F</u>	<u>131°F</u>
10	Control	0.693	0.652
	4 (0.5)	0.681	0.461
	1 (0.5)	0.317	0.331

**TABLE XVIII**

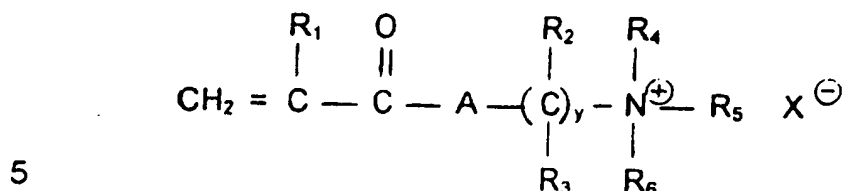
15 Effect of Dilution on Contact Angle  
Southern Liner Board Solution

	<u>Treatment No. (ppm)</u>	<u>Contact Angle</u>		
		<u>1st dilution</u>	<u>2nd dilution</u>	<u>3rd dilution</u>
20	Control	84	----	----
	4 (4)	21	59	59
	1 (4)	7	9	10

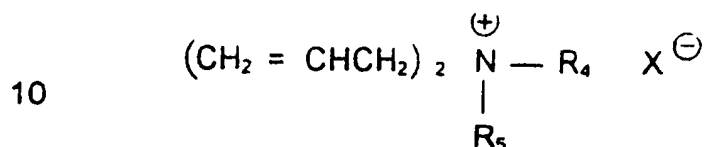
While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

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8. The method as claimed in claim 7 wherein said ethylenically unsaturated cationic monomer has the formula:



and



wherein R<sub>1</sub> in the above formula represents hydrogen or a lower, C<sub>1</sub>-C<sub>3</sub> alkyl; R<sub>2</sub> and R<sub>3</sub> independently represent hydrogen or hydroxyl; R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> independently represent lower, C<sub>1</sub>-C<sub>3</sub> alkyl or benzyl; A represents O or NH; y is 1-5 and X represents chloride or methosulfate.

9. The method as claimed in claim 8 wherein said cationic monomer is selected from the group consisting of diallyldiethylammonium chloride; diallyldimethylammonium chloride; acryloyloxyethyltrimethylammonium chloride; methacryloyloxyethyltrimethylammonium chloride; methacrylamidopropyltrimethylammonium chloride; acrylamidopropyltrimethylammonium chloride; acryloyloxyethyltrimethylammonium methosulfate; methacryloyloxyethyltrimethylammonium methosulfate; acryloyloxyethyltriethylmethylammonium chloride; methacryloyloxyethyltriethylmethylammonium chloride; methacryloyloxyethyltriethylmethylammonium chloride; and methacryloyloxyethyltriethylmethylammonium chloride.

17. The method as claimed in claim 15 wherein said polyvinyl alcohol has a molecular weight ranging from about 15,000 to about 125,000.

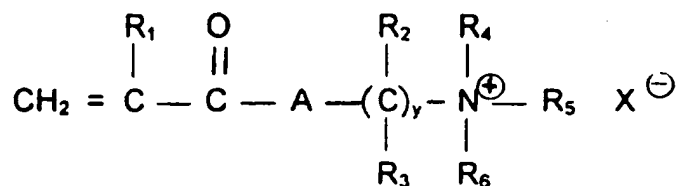
18. The method as claimed in claim 15 wherein said gelatin has a molecular weight range of about 100,000 to about 250,000.

19. The method as claimed in claim 15 wherein said cationic polymer is the reaction product between an epihalohydrin and an amine.

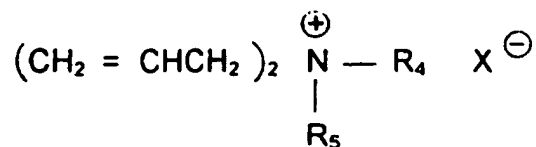
20. The method as claimed in claim 19 wherein said epihalohydrin is epichlorohydrin and said amine is selected from the group consisting of dimethylamine, ethylenediamine and a polyalkylene polyamine.

21. The method as claimed in claim 15 wherein said cationic polymer is the reaction product between acrylamide and an ethylenically unsaturated cationic monomer.

22. The method as claimed in claim 21 wherein said ethylenically unsaturated cationic monomer has the formula:



5  
and



10

27. The method as claimed in claim 15 wherein said organic contaminants are stickies deposits.

28. The method as claimed in claim 15 wherein said organic contaminants are pitch deposits.

29. The method as claimed in claim 15 wherein said surfaces are selected from the group consisting of the wire, press felts, and press rolls.

30. A composition comprising a synergistic mixture of (a) a polyvinyl alcohol having from 50 to 100% hydrolysis, (b) a high molecular weight gelatin, and (c) a cationic polymer.

31. The composition as claimed in claim 30 wherein the weight ratio of (a):(b) is about 8:1 to about 20:1 and the ratio of (b):(c) is from about 10:1 to about 0.2:1.

32. The composition as claimed in claim 30 wherein said polyvinyl alcohol has 85.5 to 87% hydrolysis.

33. The composition as claimed in claim 30 wherein said polyvinyl alcohol has a molecular weight ranging from about 15,000 to about 125,000.

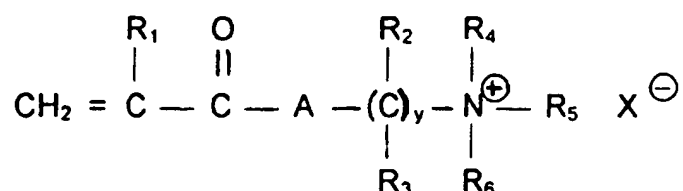
34. The composition as claimed in claim 30 wherein said gelatin has a molecular weight range of about 100,000 to about 250,000.

39. The composition as claimed in claim 38 wherein said cationic monomer is selected from the group consisting of diallyldiethylammonium chloride; diallyldimethylammonium chloride; acryloyloxyethyltrimethylammonium chloride; methacryloyloxyethyltrimethylammonium  
5 chloride; methacrylamidopropyltrimethylammonium chloride; acrylamidopropyltrimethylammonium chloride; acryloyloxyethyltrimethylammonium methosulfate; methacryloyloxyethyltrimethylammonium methosulfate; acryloyloxyethyldiethylmethylammonium chloride; methacryloyloxyethyldiethylmethylammonium chloride; methacryloyloxyethyldiethylmethyl-  
10 ammonium chloride; and methacryloyloxyethyldiethylmethylammonium chloride.

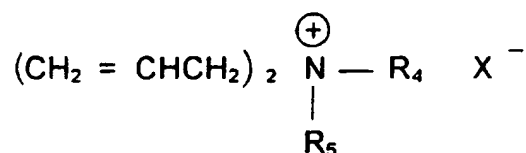
40. The composition as claimed in claim 30 wherein said cationic polymer is selected from the group consisting of polyamine and polyethyleneimine.



6. The method as claimed in claim 5 wherein said ethylenically unsaturated cationic monomer has the formula:



and



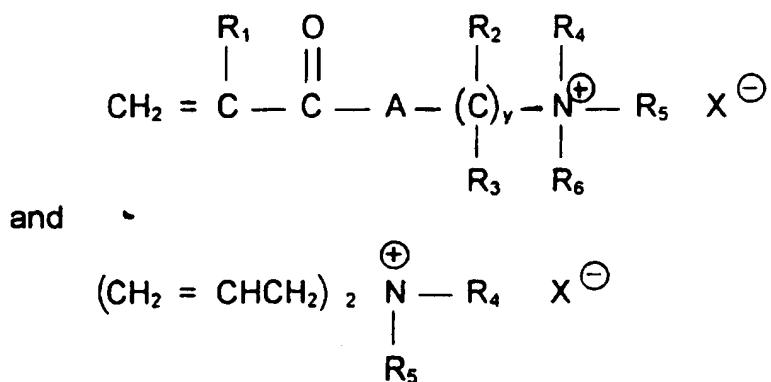
wherein R<sub>1</sub> in the above formula represents hydrogen or a lower, C<sub>1</sub>-C<sub>3</sub> alkyl; R<sub>2</sub> and R<sub>3</sub> independently represent hydrogen or hydroxyl; R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> independently represent lower, C<sub>1</sub>-C<sub>3</sub> alkyl or benzyl; A represents O or NH; y is 1-5 and X represents chloride or methosulfate.

7. The method as claimed in claim 6 wherein said cationic monomer is selected from the group consisting of diallyldiethylammonium chloride; diallyldimethylammonium chloride; acryloyloxyethyltrimethylammonium chloride; methacryloyloxyethyltrimethylammonium chloride; methacrylamidopropyltrimethylammonium chloride; acrylamidopropyltrimethylammonium chloride; acryloyloxyethyltrimethylammonium methosulfate; methacryloyloxyethyltrimethylammonium methosulfate; acryloyloxyethyltriethylmethylammonium chloride; methacryloyloxyethyltriethylmethylammonium chloride; methacryloyloxyethyltriethylmethylammonium chloride; and methacryloyloxyethyltriethylmethylammonium chloride.

14. The method as claimed in claim 13 wherein said epihalohydrin is epichlorohydrin and said amine is selected from the group consisting of dimethylamine, ethylenediamine and a polyalkylene polyamine.

15. The method as claimed in claim 11 wherein said cationic polymer is the reaction product between acrylamide and an ethylenically unsaturated cationic monomer.

16. The method as claimed in claim 15 wherein said ethylenically unsaturated cationic monomer has the formula:



wherein R<sub>1</sub> in the above formula represents hydrogen or a lower, C<sub>1</sub>-C<sub>3</sub> alkyl; R<sub>2</sub> and R<sub>3</sub> independently represent hydrogen or hydroxyl; R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> independently represent lower, C<sub>1</sub>-C<sub>3</sub> alkyl or benzyl; A represents O or NH; y is 1-5 and X represents chloride or methosulfate.

17. The method as claimed in claim 16 wherein said cationic monomer is selected from the group consisting of diallyldiethylammonium chloride; diallyldimethylammonium chloride; acryloyloxyethyltrimethylammonium chloride; methacryloyloxyethyltrimethylammonium chloride;

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/05539

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : 162/5, 168.1, 174, 199, DIG. 4; 252/351, 352, 356, 357.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/5, 168.1, 174, 199, DIG. 4; 252/351, 352, 356, 357.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,871,424 A (DREISBACH et al) 03 October 1989, see entire document.	1-40
Y	US 4,995,944 A (ASTON et al) 26 February 1991, see entire document.	1-40
Y	CASEY. J.P. Pulp and Paper Chemistry and Chemical Technology. 1961. Vol. 3. 2nd Edition. pages 1587-1588.	1-40

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Facsimile No. (703) 305-3230

Authorized officer

DONALD E. CZAJA

Telephone No. (703) 305-0651